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**Frequency Comb Spectroscopy - From IR To XUV**

**Jun Ye**  
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**Final Report**

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## Final report to AFOSR on FA9550-12-1-0078, "Frequency Comb Spectroscopy - From IR To XUV"

Principal Investigator: Jun Ye, JILA, University of Colorado, Boulder, Colorado

The development of the optical frequency comb (a spectrum consisting of a series of evenly spaced lines) has revolutionized metrology and precision spectroscopy owing to its ability to provide a precise and direct link between microwave and optical frequencies. A further advance in frequency comb technology is the generation of frequency combs in the extreme-ultraviolet spectral range by means of high-harmonic generation in a femtosecond enhancement cavity. Until now, combs produced by this method have lacked sufficient power for applications, a drawback that has also hampered efforts to observe phase coherence of the high-repetition-rate pulse train produced by high-harmonic generation, which is an extremely nonlinear process. The Ye group has recently demonstrated the generation of extreme ultraviolet frequency combs, reaching wavelengths of 40 nanometers, by coupling a high-power near-infrared frequency comb to a robust femtosecond enhancement cavity. These combs are powerful enough for us to observe single-photon spectroscopy signals for both an argon transition at 82 nm and a neon transition at 63 nm, thus confirming the combs' coherence in the extreme ultraviolet. The absolute frequency of the argon transition has been determined by direct frequency comb spectroscopy. The resolved ten-megahertz linewidth of the transition, which is limited by the temperature of the argon atoms, is unprecedented in this spectral region and places a stringent upper limit on the linewidth of individual comb teeth. Owing to the lack of continuous-wave lasers, extreme-ultraviolet frequency combs are at present the only promising route to extending ultrahigh-precision spectroscopy to the spectral region below 100 nm. At such wavelengths there is a wide range of applications, including the spectroscopy of electronic transitions in molecules, experimental tests of bound-state and many-body quantum electrodynamics in singly ionized helium and neutral helium, the development of next-generation 'nuclear' clocks and searches for variation of fundamental constants using the enhanced sensitivity of highly charged ions.

Unlike visible light, radiation in the extreme ultraviolet (XUV) has traditionally lacked long-term phase coherence and high spectral resolution, limiting its use for high resolution spectroscopy and precision measurement in this spectral region. Recent development of XUV frequency comb in the Ye group has demonstrated that spectral resolution at the MHz-level can be obtained. In 2013, we demonstrated that the phase coherence of the XUV comb can be improved by more than 6 orders of magnitude, achieving sub-Hz spectral resolution, corresponding to coherence time  $> 1$  s, in the XUV region. By leveraging the phase coherence of optical frequency combs and high harmonic generation, we have created two XUV frequency combs for a direct heterodyne beat measurement. We identified various noise contributions to the obtainable comb linewidth in the XUV. This work establishes the ability of creating highly phase stable radiation in the XUV with performance rivaling that of visible light. This capability is essential for future work of high-resolution spectroscopy in the XUV and for the use of frequency metrology tools to probe physics at the attosecond time scale.

Using the same femtosecond enhancement cavity approach we accomplished another important milestone in 2014, namely the use of frequency comb for high field molecular alignment and high harmonic generation. This marks a major triumph of extending optical frequency comb technology towards applications in the realm of strong-field physics in molecular systems. In this work, we used our extreme ultraviolet frequency comb system to demonstrate a new capability of performing high-repetition rate field-free molecular alignment, a tool widely used in strong-field physics, and high-order harmonic generation in the aligned molecular sample. The femtosecond enhancement cavity technique pioneered by our group was utilized to achieve a repetition rate nearly five orders of magnitude higher than standard systems on molecular alignment and HHG. This approach has allowed us to observe interesting phenomena in the molecule-field interaction, such as the rotational modulation of the driving field. Precise measurements of this molecule-field interaction will be vital for future studies of high-order harmonic generation and strong-field physics associated with molecules.

The Ye group has also successfully achieved a quantum-noise-limited absorption sensitivity of  $1.7 \times 10^{-12} \text{ cm}^{-1}$  per spectral element at 400 s of acquisition time with cavity-enhanced frequency comb spectroscopy, the highest demonstrated for a comb-based technique. The system comprises a frequency comb locked to a high-finesse cavity and a fast-scanning Fourier transform spectrometer with an ultralow-noise autobalancing detector. Spectra with a signal-to-noise ratio above 1000 and a resolution of 380 MHz are acquired within a few seconds. The measured absorption line shapes are in excellent agreement with theoretical predictions. The Ye group has also demonstrated the first cavity-enhanced optical frequency comb spectroscopy in the mid-infrared wavelength region and reported the sensitive real-time trace detection of hydrogen peroxide in the presence of a large amount of water. The experimental apparatus is based on a mid-infrared optical parametric oscillator synchronously pumped by a high power Yb: fiber laser, a high finesse broadband cavity, and a fast-scanning Fourier transform spectrometer with auto-balancing detection. The comb spectrum with a bandwidth of 200 nm centered around  $3.76 \mu\text{m}$  is simultaneously coupled to the cavity and both degrees of freedom of the comb, i.e., the repetition rate and carrier envelope offset frequency, are locked to the cavity to ensure stable transmission. The auto-balancing detection scheme reduces the intensity noise by a factor of 300, and a sensitivity of  $5.4 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  with a resolution of 800 MHz is achieved (corresponding to  $6.9 \times 10^{-11} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  per spectral element for 6000 resolved elements). This yields a noise equivalent detection limit for hydrogen peroxide of 8 parts-per-billion (ppb); in the presence of 2.8% of water the detection limit is 130 ppb. Spectra of acetylene, methane and nitrous oxide at atmospheric pressure are also presented, and a line shape model is developed to simulate the experimental data. This development has stimulated a strong interest in the biomedical community on the unique capabilities of frequency comb spectroscopy.

Continuing to expand on the direction of frequency comb spectroscopy in mid-infrared, in 2013 we demonstrated the use of comb spectroscopy for dynamic analysis of chemical reactions. Quantitative measurements in chemical kinetics require unambiguous determinations of reactant, intermediate, and product concentrations on time scales faster

than the reaction rate. Direct absorption spectroscopy in the mid-infrared (mid-IR) can fulfill the quantitative requirement, often with high detection sensitivities, thanks to strongly absorbing fundamental molecular vibrations. We now introduce time-resolved frequency comb spectroscopy (TRFCS) and demonstrate a novel transient absorption technique in the mid-IR for the study of chemical kinetics on the  $\mu\text{s}$  timescale. With noise-equivalent absorption sensitivity of  $2.0 \times 10^{-9} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  per spectral element over a  $65 \text{ cm}^{-1}$  instantaneous bandwidth, we apply TRFCS to the study of time-resolved absorption of the deuterated hydroxyformyl radical *trans*-DOCO, an important short-lived intermediate in the OH + CO reaction path. Directly after its initial formation via photolysis of a chemical precursor we measure the absolute *trans*-DOCO concentration and its subsequent reaction rate at time resolution of 25  $\mu\text{s}$ .

#### Publications:

- [1] A. Cingöz, Yost, D. C. , Allison, T. K. , Ruehl, A. , Fermann, M. E. , Hartl, I. , and Ye, J. , “Direct frequency comb spectroscopy in the extreme ultraviolet”, *Nature*, vol. 482, no. 7383, pp. 68 - 71, 2012.
- [2] C. Benko, Ruehl, A. , Martin, M. J. , Eikema, K. S. E. , Fermann, M. E. , Hartl, I. , and Ye, J. , “Full phase stabilization of a Yb: fiber femtosecond frequency comb via high-bandwidth transducers”, *Optics Letters*, vol. 37, no. 12, pp. 2196-2198 , 2012.
- [3] M. Golkowski, Leszczynski, J. , Plimpton, R. S. , Maslowski, P. , Foltynowicz, A. , Ye, J. , and McCollister, B. , “Hydrogen-Peroxide-Enhanced Nonthermal Plasma Effluent for Biomedical Applications”, *IEEE Transactions on Plasma Science*, vol. 40, no. 8, pp. 1984 - 1991, 2012.
- [4] L. Nugent-Glandorf, Neely, T. , Adler, F. , Fleisher, A. J. , Cossel, K. C. , Bjork, B. , Dinneen, T. , Ye, J. , and Diddams, S. A. , “Mid-infrared virtually imaged phased array spectrometer for rapid and broadband trace gas detection”, *Optics Letters*, vol. 37, no. 15, pp. 3285-3287, 2012.
- [5] A. Foltynowicz, Masłowski, P. , Fleisher, A. J. , Bjork, B. J. , and Ye, J. , “Cavity-enhanced optical frequency comb spectroscopy in the mid-infrared application to trace detection of hydrogen peroxide”, *Applied Physics B*, vol. 110, pp. 163–175, 2013.
- [6] P. Masłowski, Cossel, K. C. , Foltynowicz, A. , and Ye, J. , *Springer Series in Optical Sciences: Cavity-Enhanced Spectroscopy and Sensing: Cavity-Enhanced Direct Frequency Comb Spectroscopy*, vol. 179. Springer, Berlin Heidelberg, 2014, pp. 271 - 321.
- [7] A. J. Fleisher, Bjork, B. J. , Bui, T. Q. , Cossel, K. C. , Okumura, M. , and Ye, J. , “Mid-Infrared Time-Resolved Frequency Comb Spectroscopy of Transient Free Radicals”, *The Journal of Physical Chemistry Letters*, vol. 5, no. 13, pp. 2241 - 2246, 2014.

[8] C. Benko, Allison, T. K. , Cingöz, A. , Hua, L. , Labaye, F. , Yost, D. C. , and Ye, J. , “Extreme ultraviolet radiation with coherence time greater than 1 s”, *Nature Photonics*, vol. 8, pp. 530 – 536 , 2014.

[9] C. Benko, Hua, L. , Allison, T. K. , Labaye, F. , and Ye, J. , “Cavity-Enhanced Field-Free Molecular Alignment at a High Repetition Rate”, *Physical Review Letters*, vol. 114, p. 153001, 2015.

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**Abstract**

The proposed work explores the frontiers of coherent light-matter interactions in spectral regions that have yet to witness such advanced developments. Optical frequency combs offer enormous potential in the detection and control of atoms and molecules by combining high sensitivity, precise frequency control, broad spectral coverage, and high resolution in one experimental platform. Sensitive and multiplexed trace gas detection via cavity-enhanced direct frequency comb spectroscopy (CE-DFCS) has been demonstrated for various molecules and applications, as well as precise quantum control of atomic transitions via coherent pulse accumulations. Future spectroscopic and quantum control capabilities will be created by developing frequency comb sources in the deep ultraviolet and mid-infrared spectral regions. We emphasize that these distant spectral regions will in fact be coherently connected, creating a new frontier for coherent spectroscopy and broad bandwidth high-resolution quantum control of molecular dynamics. We will also bring revolutionary impact on precision metrology and ultrafast science from the visible spectral region to the next exciting frontier of extreme ultraviolet (XUV) by developing powerful XUV frequency combs.

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- [3] M. Golkowski, Leszczynski, J. , Plimpton, R. S. , Maslowski, P. , Foltynowicz, A. , Ye, J. , and McCollister, B. , "Hydrogen-Peroxide-Enhanced Nonthermal Plasma Effluent for Biomedical Applications", IEEE Transactions on Plasma Science, vol. 40, no. 8, pp. 1984 - 1991, 2012.
- [4] L. Nugent-Glandorf, Neely, T. , Adler, F. , Fleisher, A. J. , Cossel, K. C. , Bjork, B. , Dinneen, T. , Ye, J. , and Diddams, S. A. , "Mid-infrared virtually imaged phased array spectrometer for rapid and broadband trace gas detection", Optics Letters, vol. 37, no. 15, pp. 3285-3287, 2012.
- [5] A. Foltynowicz, Masłowski, P. , Fleisher, A. J. , Bjork, B. J. , and Ye, J. , "Cavity-enhanced optical frequency comb spectroscopy in the mid-infrared application to trace detection of hydrogen peroxide", Applied Physics B, vol. 110, pp. 163–175, 2013.
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- [7] A. J. Fleisher, Bjork, B. J. , Bui, T. Q. , Cossel, K. C. , Okumura, M. , and Ye, J. , "Mid-Infrared Time-Resolved Frequency Comb Spectroscopy of Transient Free Radicals", The Journal of Physical Chemistry Letters, vol. 5, no. 13, pp. 2241 - 2246, 2014.
- [8] C. Benko, Allison, T. K. , Cingöz, A. , Hua, L. , Labaye, F. , Yost, D. C. , and Ye, J. , "Extreme ultraviolet radiation with coherence time greater than 1 s", Nature Photonics, vol. 8, pp. 530 – 536 , 2014.
- [9] C. Benko, Hua, L. , Allison, T. K. , Labaye, F. , and Ye, J. , "Cavity-Enhanced Field-Free Molecular Alignment at a High Repetition Rate", Physical Review Letters, vol. 114, p. 153001, 2015.

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